

Phase competitions in epitaxial $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3/\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ superlattices

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We studied the charge-orbital ordering in the superlattice of charge-ordered insulating $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and ferromagnetic metallic $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ by resonant soft x-ray diffraction. A temperature-dependent incommensurability is found in the orbital order. In addition, a large hysteresis is observed that is caused by phase competition between insulating charge ordered and metallic ferromagnetic states. No magnetic phase transitions are observed in contrast to bulk, confirming the unique character of the superlattice. The deviation from the commensurate orbital order can be directly related to the decrease of ordered-layer thickness that leads to a decoupling of the orbital-ordered planes along the c axis.

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Hole-doped perovskite manganites $RE_{1-x}A_x\text{MnO}_3$, where RE is a rare-earth ($RE = \text{La}, \text{Nd}, \text{Pr}$) and A is an alkaline-earth atom ($A = \text{Sr}, \text{Ba}, \text{Ca}$) have attracted much attention because they exhibit remarkable physical properties such as colossal magnetoresistance (CMR) and complex electronic ordering phenomena [1–8]. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ has a large bandwidth and a ferromagnetic metallic (FM) ground state is realized for approximately $0.2 < x < 0.5$ [9]. Most of the half-doped manganites ($x \simeq 0.5$) with a small bandwidth exhibit the so-called “CE-type” charge and orbitally ordered (CO/OO) insulating and antiferromagnetic (AF) ordering with alternating Mn^{3+} and Mn^{4+} states within the (001) plane in the form of stripes [10]. This ordering competes with the FM phase. Phase competition between ordered phases is an interesting phenomenon and leads to intriguing behaviors such as CMR and nanometer-scale phase separation. These ordering phenomena lead to symmetry lowering and a doubling of the unit cell, which results in superlattice reflections observable with different scattering techniques. For higher doping levels $x > 0.5$, the doping leads to orderings, that are incommensurate, with ordering wave vector proportional to the doping concentration [11, 12].

In recent years, epitaxially grown films of manganites have been extensively studied. It was found that $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films are ferromagnetic for approximately $0.2 < x < 0.5$, almost the same as the bulk [13, 14]. Half-doped manganite thin films remain often charge and orbitally ordered, but physical properties might depend on the strain, that is, the lattice constant

and orientation of the substrates. A transition between CO and FM states was observed in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ thin films on SrTiO_3 substrates only when the substrate orientation was (011) [15, 16]. Also in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ thin films, epitaxial strain strongly affects the electronic properties, and the thin films grown epitaxially on $(\text{LaAlO}_3)_{0.3}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.7}$ (LSAT) (011) substrates exhibit a CO transition around 220 K, similar to bulk samples [17].

Interesting phenomena occur when these two systems are brought in direct contact. Results on such stackings has recently been reported by Nakamura *et al.* [18]. They fabricated superlattices of FM $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (LSMO) and CO $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (PCMO) on LSAT (011) substrates [18]. They found that they could control the phase boundary at the interface between the ferromagnetic LSMO and the AF and CO/OO PCMO by the application of magnetic fields or changing the individual layer thicknesses. In addition, they observed superlattice reflections indicative for the structural distortions induced by the charge and orbital order in these systems. Particularly interesting is the case of having equal thicknesses. In that case the reflections exhibit a strong hysteresis behavior even in zero magnetic field, a direct evidence for the first-order phase transition between these competing phases.

To gain more insight to these problems of phase transitions and phase competitions, we investigated the charge-orbital ordering in [PCMO (5 layers)/LSMO (5 layers)]₁₅ superlattices by resonant soft x-ray diffraction. This technique combines the sensitivity of the $\text{Mn } 2p \rightarrow 3d$ electronic transition to the electronic and magnetic properties of the transition metal $3d$ states with the sensitivity to long range order of diffraction. It has been used to disentangle magnetic and orbital ordering phenomena in manganites [19–29], and is extremely sensitive to even

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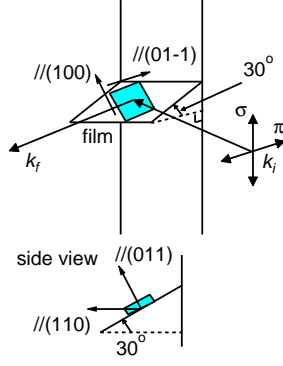


FIG. 1: (Color online): The experimental geometry having the $[110]$ axis of the PCMO/LSMO superlattice in the scattering plane.

small details in the electronic orderings. It is especially sensitive to the magnetic structures in thin films [27–30], and has recently been used to study effect of imprinting magnetic and electronic information in epitaxially grown PCMO films [28]. In the present study we find a significant hysteresis behavior of the superlattice reflection that is sensitive to the orbital order of the Mn $3d$ states. In addition the system shows a clear temperature dependence of the ordering wave vector with hysteresis behaviors. The temperature dependent incommensurability in the orbital ordering can be related to the change of orbital coupling through the FM metallic layer centered around the LSMO layer.

[PCMO (5 layers)/LSMO (5 layers)]₁₅ superlattices were grown on the (011) surface of an LSAT substrate by pulsed laser deposition. The details of the sample fabrication were described elsewhere [18]. Resonant soft x-ray diffraction experiments were performed on the RESOXS end station [31] at the surface-interface microscopy (SIM) beam line [32] of the Swiss Light Source of the Paul Scherrer Institut, Switzerland. The experimental geometry is shown in Fig. 1, which is the same as that in Ref. [29]. A continuous helium-flow cryostat allows measurements between 10 and 300 K. The experiments were performed in the out-of-focus mode with a beam of approximately $2 \times 2 \text{ mm}^2$.

Figure 2 shows the q dependence of the $(hh0)$ reflection for various temperatures at the Mn $2p_{3/2}$ edge (643 eV) for both π and σ incoming x-ray polarizations. This reflection has been studied in detail in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ bulk manganites and epitaxial grown films [22, 24, 26, 28, 29], and has been shown to be sensitive to both the orbital and magnetic orderings of the systems. The temperature dependence of this reflection in a heating run (panels (a) and (b)) significantly deviates from that in a cooling run (panels (c) and (d)). The reflection appears below ~ 200 K, which is slightly lower than the CO transition temperature of 220 K in the pure PCMO thin film [17]. There is almost no difference between π (a, c) and σ (b, d) polarizations. The tem-

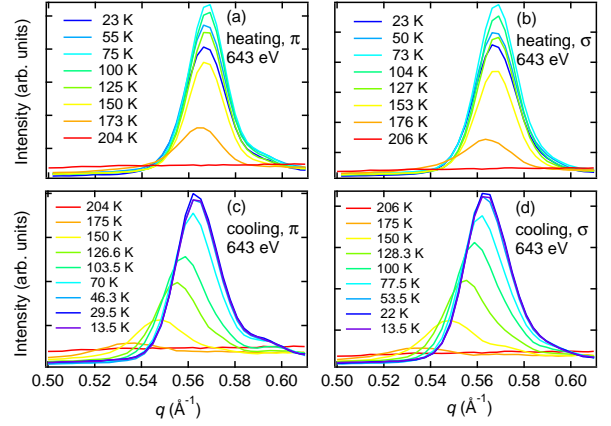


FIG. 2: (Color online): Temperature dependence of the $(hh0)$ peak. Panels (a) and (b) ((c) and (d)) were measured in the heating (cooling) cycle. Incident x-ray polarizations were π in (a) and (c) and σ (b) and (d). All the data were taken at $h\nu = 643 \text{ eV}$ (Mn $2p_{3/2} \rightarrow 3d$ absorption edge).

perature variation of the corresponding peak intensity, the full width at half maximum (FWHM), and positions is summarized in Fig. 3. In all of these quantities, a large hysteresis is observed between cooling and heating cycles. The peak intensity monotonically increases for decreasing temperatures in contrast to the heating cycle, where, interestingly, it first increases and then decreases before it disappears around 200 K. This is related to both the temperature dependence of the position and FWHM of the reflection. The peak position is incommensurate and temperature dependent in the full range of the cooling cycle. In contrast, the position remains frozen until temperatures of approximately 170 K for the heating cycle. As the peak position of this reflection type has been found to be related with the doping level [25], it might reflect an *effective* doping in the PCMO layer, which is slightly larger than 0.5 and is temperature dependent.

The width also shows an interesting behavior. When the FWHM is minimal, the intensity is maximal. In the heating cycle, this is the case for temperatures between 50 and 150 K. This shows that there is a clear connection among the improved order (maximal intensity), the correlation (maximal correlation length), and the largest h . To test if this relation is quantitatively the same for cooling and heating cycles, we show in panel (d) the FWHM as a function of peak position. Although the width is linearly dependent on the peak position for both the cooling and the heating cycles, the slope of the two is significantly different. Since the hysteresis behavior in all three parameters between heating and cooling cycles must be caused by dynamics in orbital and magnetic order, the same origin is expected to be responsible for differences in the slope.

Figure 4 shows the spectral shape of the $(hh0)$ reflection in the vicinity of the Mn $2p$ edges at 170 K (a)

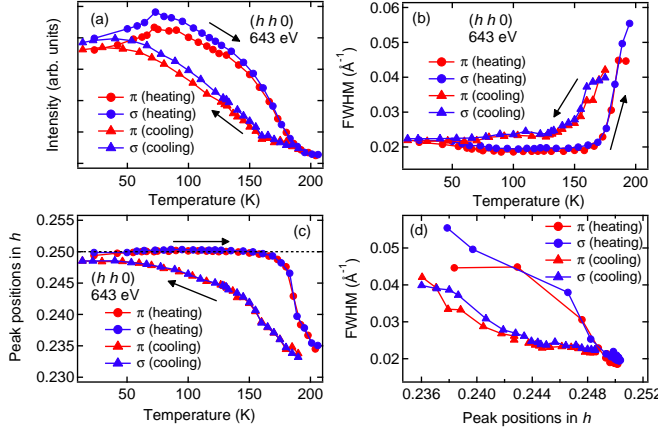


FIG. 3: (Color online): Temperature dependence of the $(hh0)$ peak intensity (a), width (b), and positions (c). In panel (d), the peak width is plotted as a function of peak positions.

and 23 K (b). There is no polarization dependence at both temperatures. In addition, the spectral shape is identical at these two temperatures and very similar to the pure orbital scattering of the analogue reflection in bulk $\text{La}_{1.5}\text{Sr}_{0.5}\text{MnO}_4$ [20, 21, 23] and the pure PCMO thin film [29]. In other words, we find no indication of magnetic scattering in the superlattice, in contrast to the pure PCMO thin film [29]. There, the resonant soft x-ray diffraction revealed two magnetic transitions; $T_N = 150$ K and $T_2 = 75$ K. The magnetic intensity of the $(hh0)$ reflection in the film and the bulk can be directly related to a spin canting of the Mn spins along the c axis, which is clearly absent in the superlattice. Nevertheless, the intensity maximum in the heating cycle occurring around 70 K coincides with the magnetic transition of the pure PCMO thin film. In bulk $(\text{La},\text{Pr},\text{Ca})\text{MnO}_3$ systems, this 70 K magnetic transition is much more pronounced [33] and is believed to be caused by a phase separation between FM and AF phases with glassy character at low temperatures. Such a phase transition would also be directly visible in the observed orbital reflection intensities. The difference between the PCMO thin film and the corresponding bulk material indicates that the epitaxial strain affects the magnetism in thin films [29]. The observation of the 70 K transition in the orbital signal in the superlattice is an indirect evidence that the superlattice is AF with spins lying fully in the ab -plane, as observed by neutron diffraction on PCMO bulk samples [10].

Combining our data with the results from Ref. [18] leads now to the following picture. The proposed phase separation between the FM LSMO layers and the orbital ordered AF PCMO layers is supported by the observation of both the ferromagnetic moment [18] and the orbital reflection. The sharp reflection with a correlation length of the order of the total film thickness indicates that the correlation between the CO/OO states perfectly bridges the

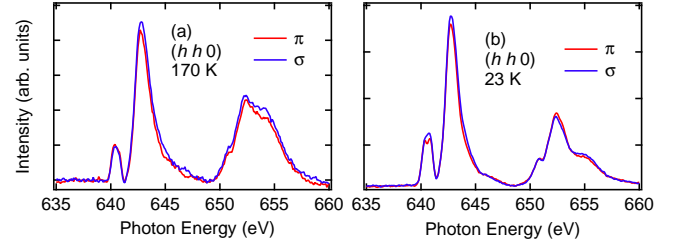


FIG. 4: (Color online): Intensity of the $(hh0)$ peak as a function of photon energies at the Mn $2p \rightarrow 3d$ absorption edge at 170 K (a) and 23 K (b).

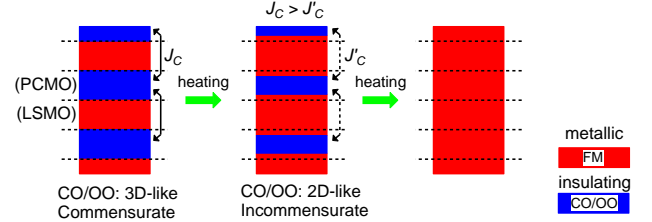


FIG. 5: (Color online): Real-space sketches of phase separations between FM and CO states.

FM layers built in between. This is visualized in Fig. 5. This orbital coupling bridging over the FM LSMO layers becomes weak when the temperature increases because the interface CO/OO states disappear first, leading to an effective increase of the separation of the CO/OO layers (see Fig. 5). The proximity effect leads to a slight change of the overall doping in the CO/OO layers, which can explain the change in the ordering wave vectors. This affects also the correlation length. This behavior is similar to that found for $2/3$ doped $\text{Tb}_{0.66}\text{Ca}_{0.33}\text{BaMn}_2\text{O}_6$ [25], where, due to the A-site order in layers, a similar two-dimensional (2D) character exists in the bulk (though with much shorter distances). Also in these systems, a competition between FM/AF ordering exists, and for a wide range of doping a change of ordering vector and correlation length has been interpreted in terms of a decoupling between the orbital-ordered layers along the c -axis.

In summary, we performed resonant soft x-ray diffraction measurements on the superlattice of charge-ordered insulating PCMO and ferromagnetic metallic LSMO to study the charge-orbital ordering in PCMO layers. We found clear differences from the pure PCMO and LSMO thin films. A large hysteresis was observed due to the phase competition and different magnetic ordering in the superlattice. We found distinct changes of the ordering wave vector and the correlation length connected to 2D characters of the system. These observations give indication for an “effective” doping caused by the proximity effect, resulting in a model of phase separations between FM and CO/OO states.

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- [1] M. Imada, A. Fujimori, and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).
 - [2] A. P. Ramirez, *J. Phys.: Condens. Mat.* **9**, 8171 (1997).
 - [3] Y. Tokura and N. Nagaosa, *Science* **288**, 462 (2000).
 - [4] C. N. R. Rao, A. Arulraj, A. K. Cheetham, and B. Raveau, *J. Phys.: Condens. Mat.* **12**, R83 (2000).
 - [5] W. Prellier, P. Lecoeur, and B. Mercey, *J. Phys.: Condens. Mat.* **13**, R915 (2001).
 - [6] E. Dagotto, T. Hotta, and A. Moreo, *Phys. Rep.* **344**, 1 (2001).
 - [7] A. M. Haghir-Gosnet and J. P. Renard, *J. Phys. D: Appl. Phys.* **36**, R127 (2003).
 - [8] Y. Tokura, *Rep. Prog. Phys.* **69**, 797 (2006).
 - [9] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, *Phys. Rev. B* **51**, 14103 (1995).
 - [10] Z. Jirak, S. Krupicka, Z. Simsa, M. Dlouha, and S. Vratislav, *J. Magn. Magn. Mater.* **53**, 153 (1985).
 - [11] G. C. Milward, M. J. Calderon, and P. B. Littlewood, *Nature* **433**, 607 (2005).
 - [12] S. Shimomura, T. Tonegawa, K. Tajima, N. Wakabayashi, N. Ikeda, T. Shobu, Y. Noda, Y. Tomioka, and Y. Tokura, *Phys. Rev. B* **62**, 3875 (2000).
 - [13] M. Izumi, Y. Konishi, T. Nishihara, S. Hayashi, M. Shinohara, M. Kawasaki, and Y. Tokura, *Appl. Phys. Lett.* **73**, 2497 (1998).
 - [14] K. Horiba, A. Chikamatsu, H. Kumigashira, M. Oshima, N. Nakagawa, M. Lippmaa, K. Ono, M. Kawasaki, and H. Koinuma, *Phys. Rev. B* **71**, 155420 (2005).
 - [15] M. Nakamura, Y. Ogimoto, H. Tamaru, M. Izumi, and K. Miyano, *Appl. Phys. Lett.* **86**, 182504 (2005).
 - [16] Y. Wakabayashi, D. Bizen, H. Nakao, Y. Murakami, M. Nakamura, Y. Ogimoto, K. Miyano, and H. Sawa, *Phys. Rev. Lett.* **96**, 017202 (2006).
 - [17] D. Okuyama, M. Nakamura, Y. Wakabayashi, H. Itoh, R. Kumai, H. Yamada, Y. Taguchi, T. Arima, M. Kawasaki, and Y. Tokura, *Appl. Phys. Lett.* **95**, 152502 (2009).
 - [18] M. Nakamura, D. Okuyama, J. S. Lee, T. Arima, Y. Wakabayashi, R. Kumai, M. Kawasaki, and Y. Tokura, *Adv. Mater.* **22**, 500 (2010).
 - [19] S. B. Wilkins, P. D. Hatton, M. D. Roper, D. Prabhakaran, and A. T. Boothroyd, *Phys. Rev. Lett.* **90**, 187201 (2003).
 - [20] S. B. Wilkins, P. D. Spencer, P. D. Hatton, S. P. Collins, M. D. Roper, D. Prabhakaran, and A. T. Boothroyd, *Phys. Rev. Lett.* **91**, 167205 (2003).
 - [21] S. S. Dhesi, A. Mirone, C. D. Nadai, P. Ohresser, P. Bencok, N. B. Brookes, P. Reutler, A. Revcolevschi, A. Tagliaferri, O. Toulemonde, and G. van der Laan, *Phys. Rev. Lett.* **92**, 056403 (2004).
 - [22] K. J. Thomas, J. P. Hill, S. Grenier, Y.-J. Kim, P. Abbamonte, L. Venema, A. Rusydi, Y. Tomioka, Y. Tokura, D. F. McMorrow, G. Sawatzky, and M. van Veenendaal, *Phys. Rev. Lett.* **92**, 237204 (2004).
 - [23] S. B. Wilkins, T. A. W. Beale, P. D. Hatton, J. A. Purton, P. Bencok, D. Prabhakaran, and A. T. Boothroyd, *New J. Phys.* **7**, 80 (2005).
 - [24] U. Staub, M. Garcia-Fernandez, Y. Bodenthin, V. Scagnoli, R. A. D. Souza, M. Garganourakis, E. Pomjakushina, and K. Conder, *Phys. Rev. B* **79**, 224419 (2009).
 - [25] M. Garcia-Fernandez, U. Staub, Y. Bodenthin, V. Scagnoli, V. Pomjakushin, S. W. Lovesey, A. Mirone, J. Herrero-Martin, C. Piamonteze, and E. Pomjakushina, *Phys. Rev. Lett.* **103**, 097205 (2009).
 - [26] S. Y. Zhou, Y. Zhu, M. C. Langner, Y.-D. Chuang, P. Yu, W. L. Yang, A. G. C. Gonzalez, N. Tahir, M. Rini, Y.-H. Chu, R. Ramesh, D.-H. Lee, Y. Tomioka, Y. Tokura, Z. Hussain, and R. Schoenlein, *Phys. Rev. Lett.* **106**, 186404 (2011).
 - [27] H. Wadati, J. Okamoto, M. Garganourakis, V. Scagnoli, U. Staub, Y. Yamasaki, H. Nakao, Y. Murakami, M. Mochizuki, M. Nakamura, M. Kawasaki, and Y. Tokura, *Phys. Rev. Lett.* **108**, 047203 (2012).
 - [28] M. Garganourakis, V. Scagnoli, S. W. Huang, U. Staub, H. Wadati, M. Nakamura, V. A. Guzenko, M. Kawasaki, and Y. Tokura, *Phys. Rev. Lett.* **109**, 157203 (2012).
 - [29] H. Wadati, J. Geck, E. Schierle, R. Sutarto, F. He, D. G. Hawthorn, M. Nakamura, M. Kawasaki, Y. Tokura, and G. A. Sawatzky, *arXiv:1111.4725*.
 - [30] V. Scagnoli, U. Staub, A. M. Mulders, M. Janousch, G. I. Meijer, G. Hammerl, J. M. Tonnerre, and N. Stojic, *Phys. Rev. B* **73**, 100409(R) (2006).
 - [31] U. Staub, V. Scagnoli, Y. Bodenthin, M. Garcia-Fernandez, R. Wetter, A. M. Mulders, H. Grimmer, and M. Horisberger, *J. Synchrotron Radiat.* **15**, 469 (2008).
 - [32] U. Flechsig, J. AlsNielsen, A. Jaggi, J. Krempasky, P. Oberta, S. Spielmann, and J. F. van der Veen, *AIP Conf. Proc.* **1234**, 653 (2010).
 - [33] W. Wu, C. Israel, N. Hur, S. Park, S.-W. Cheong, and A. de Lozanne, *Nat. Mater.* **5**, 881 (2005).